STUDIES OF COAL AND CHAR PROPERTIES

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INTRODUCTION

A thermodynamic data base is required both for the understanding and the proper design of processes utilizing coal and coal products. Since it is impractical to acquire the necessary data for each process and for each individual coal, it is important to establish predictive correlations between the physical and chemical parameters of the materials and their thermodynamic properties.

Heat capacity data can be used to calculate the variation of the thermodynamic properties, H,S.G, etc. with temperature. Conventional correlations of the heat capacities rely on the additivity approach, namely, that the total heat capacity of a dry coal is a matter, and inorganics (1,2,3). The correlation is successful in the sense that heat load calculations within 20% are possible.

The method has serious shortcomings inasmuch as it does not take into account the thermal history of the chars, the variability of the char structure with the rank of the parent coal and the interactions between the organic and inorganic components of the coal and/or of the char. Factors which affect the heat capacity of coals are:

- o The rank and inorganic matter content of the coal;
- o The moisture content;
- o The aging history of the coal sample.

Factors which affect the heat capacity of chars are:

- o The rank and inorganic matter content of the parent coal;
- o The gaseous atmosphere present during pyrolysis;
- o The thermal history of the char.

The history of a char is determined by:

- o The pyrolysis temperature;
- o The rate at which the coal temperature is increased from ambient to pyrolysis temperature;
- o The residence time of the char at the pyrolysis temperature.

Available data (4,5,6,7,8,9) for chars and coals cover limited temperature ranges and the thermal histories and compositions of the char samples are often ill-defined or unavailable. Thus, it was not possible to derive a universal correlation for the heat capacitie, taking the listed factors into account.

In an attempt to establish a thermodynamic data base for coals and chars and to assess the relative importance and effect of the factors listed, on the heat capacity, extensive work was undertaken and is continuing at City College (10,11,12,13). In this presentation we will limit ourselves to the discussion of results on chars.

EXPERIMENTAL DETAILS

A suite of samples was prepared for experimental work in a systematic manner. Three coals of different rank and petrography were used as starting materials. These selected 'parents' were a North Dakota lignite, an Illinois No. 6 HVB sub-bituminous, and a Virginia HVA sub-bituminous coal. The carbon content of these coals range from 63 to 73 weight percent (dry basis). The coals were ground in a ball mill to finer than 250 mesh. Half of the coal grounds were demineralized using the acid wash procedure (14). The other half was used without further treatment.

The pyrolysis was done in an inert atmosphere, by sweeping the furnace with nitrogen gas (1-SCFM flow rate). The samples were heated to the pyrolysis temperature with a relatively slow heating rate of 5°C per minute. Both pyrolysis temperature and residence time at temperature were used as variables for establishing thermal histories for the chars. Pyrolysis temperatures used were 500°C, 700°C, 900° C and 1100°C. Residence times were 0.1, 1, 2, and 24 hours. The char and coal samples were characterized by composition, porosity, pore size distribution and X-ray diffraction.

Heat capacity data were collected between 75K and 300K in a cryostat which was modified in order to use the adiabatic shield technique of calorimetry (15,16). To eliminate the contributions of adsorbed water to the specific heat, the experimental samples were vacuum dried at 110°C prior to loading into the calorimeter. The calorimeter was kept constantly under vacuum during the experimental runs. Each specimen was measured at least twice in separate experimental runs. The accuracy and reproducibility of the calorimetric data, and the validity of the data reduction scheme

were checked by the measurement and the determination of the heat capacity of copper and graphite samples (17,18,19). The data is judged reliable to one percent accuracy in the temperature range of 75K to 220K.

In the 150K to 1000K range heat capacity data was collected using a Differential Scanning Calorimeter (DSC). The heat capacities were measured under an Argon atmosphere. The raw DSC data were converted into heat capacities by calibration of the instrument using a Sapphire heat capacity standard. The accuracy of the DSC data is estimated at 2 percent.

RESULTS; EFFECT OF INORGANIC PHASE

The generality of the additivity hypothesis for the heat capacity of the chars was tested by determining the heat capacities of chars prepared from untreated coals, i.e., including the inorganic matter, and from coals which have been demineralized. The experimental data are shown in Figures 1,2, and 3. It was found that for the chars prepared from Illinois and Virginia coals the total heat capacity could be expressed on a weight basis as:

$$C_s = (1-w)C_o + wC_a \qquad 1)$$

Where C_s, C_o and C_a are the heat capacities of the char, ash free organic matter and ash respectively and w is the weight fraction of ash in the char. The temperature dependence of C_a in the 75K to 300K range varies depending on the origin of the ash.

The preparation of lignite based char from untreated coal is complicated by the catalytic effect of the included inorganic matter on the pyrolysis reaction. Both the rate of pyrolysis and the structure of the char formed are affected by the presence of inorganic matter. Therefore, it is not surprising that the total heat capacity of a lignitic char does not follow the additivity hypothesis.

The contribution of the ash to the total heat capacity of the char is not trivial. On a weight basis the ash heat capacity at room temperature is about four times greater than the heat capacity of the corresponding ash free organic matter in the char.

EFFECT OF PYROLYSIS TEMPERATURE AND CHAR PARENTAGE

The dependence of the heat capacities on pyrolysis temperature and origin was examined by determination of the heat capacities of chars prepared at several pyrolysis temperatures from demineralized coals with one hour residence time at the pyrolysis temperatures. In order to compare the data on the different chars quantitatively, the measured heat capacities must be corrected for residual ash contributions and need to be converted from a per unit mass to a per mole (ash free) atom basis.

The heat capacities at a given temperature, of chars of identical thermal history, are not simply related to the rank of the parent coal. As seen in Figure 4 the lignite chars have the highest heat capacities and Virginia chars the lowest at low temperatures. However, this order is reversed at high temperatures.

In Figures 5,6, and 7 the dependence of the char heat capacities on pyrolysis temperature are shown. The behavior is again complex. On a unit mass basis the heat capacities for a char of a given parentage shows cross-overs with temperature. This phenomenon is especially pronounced for the chars originating from the higher ranked coals.

EFFECT OF RESIDENCE TIME AT PYROLYSIS TEMPERATURE

Demineralized Virginia chars prepared at 1100^{o}C were used to investigate the effect of residence time on the heat capacities. The volatile matter was effectively removed from the coal by the time the pyrolysis reactor reached the pyrolysis temperature. Thus, the only further changes that occur as a function of time are dehydrogenation and graphitization (structural ordering) of the char. The heat capacities of the chars decrease with increasing residence time up to 1 hour, then increase for a 24-hour char. We show this behavior as heat capacity isotherms in Figure 8. This is interpreted as indicating that equilibration to a final H/C ratio at the pyrolysis temperature is a fast process relative to the ordering of the char which must take place by solid phase diffusion.

CORRELATION OF THE CHAR HEAT CAPACITY WITH PHYSICAL PARAMETERS

The primary interest in this research was to find a correlation between the heat capacities and physical parameters that characterize the chars. The parameters should include, at least, the char composition and the thermal history of the chars.

The heat capacity of a solid is reasonably well-described by the Debye theory. One can invert the heat capacity C_v using the well-known relation:

$$C_v = 9R(T/\theta)^3 \int_0^{\theta/T} \frac{u^4 e^4 du}{(e^u-1)^2} \qquad 2)$$

To obtain the effective Debye temperature θ as a function of temperature T, the measured specific heat obtained at constant-pressure conditions can be used instead of the constant-volume specific heat C_v, called for by the theory, since for a solid the difference between C_p and C_v is within experimental error at least below 300K. Values of the integral in Equation 2 can be found in standard tables (20). We were able to correlate $\theta(T)$ for the chars with parentage, composition and pyrolysis temperature T_p (in ^oK).

To apply the Debye model to a char, the ordinary theory must be modified (21). Consider that the carbon and "other kinds" of atoms of the char are distributed randomly in the solid matrix. Since the chars consist of about 90% (or more) carbon atoms, only carbon-carbon and carbon-"other" atom interactions need be considered for calculation of the char vibrational frequency spectrum. If the char consisted of carbon atoms only, the spectrum would depend solely on the arrangement of the carbon atoms in the matrix. The orderliness of this arrangement depends on the pyrolysis temperature (and residence time). This suggests use of the pyrolysis temperature T_p, as a nondimensionalizing parameter to calculate θ as a dunction of a reduced temperature $T_r=T/T_p$. This allows us to compare the effective Debye temperatures for chars of the same parentage but different thermal histories.

The carbon-other atom interactions will modify the vibrational spectrum by the addition of singular vibrational modes which will add onto the spectrum in the form of Einstein-like terms. These terms should, to the lowest order, be proportional to the product of the carbon atom abundance and the "other" atom abundance.

The correlation which was found (12) to fit the suggested model, using data from 75K to 300K, is given by:

$$\theta(T_r) = \theta_o (T_r) \exp [I(T_r)/x(1-x)] \qquad 3)$$

where 1-x = the atomic fraction of carbon in the ash-free char,
$\theta_o(T_r)$ = a Debye temperature at a given value of T_r for a char consisting of carbon atoms alone;
$I(T_r)$ = an interaction parameter connecting the carbon to the "other" atoms;
θ_o and I were found by trial and error fitting of Equation 3 to the experimental data.

At the present time we are continuing the interpretive work to refine the correlation equation and to include into it the residence time dependence of the heat capacities.

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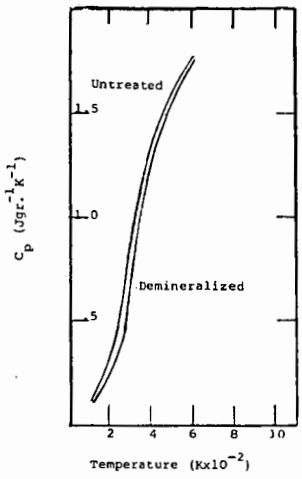

Figure 1. Illinois Char

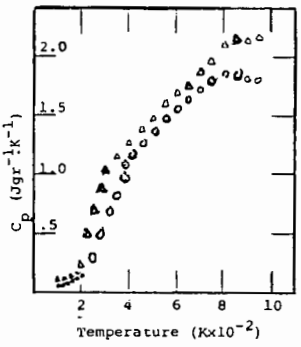

Figure 2. Virginia Chars
o Demineralized
Δ Untreated

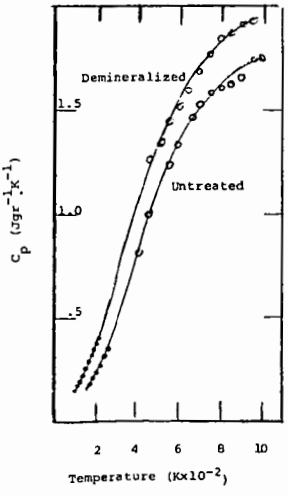

Figure 3. North Dakota Char

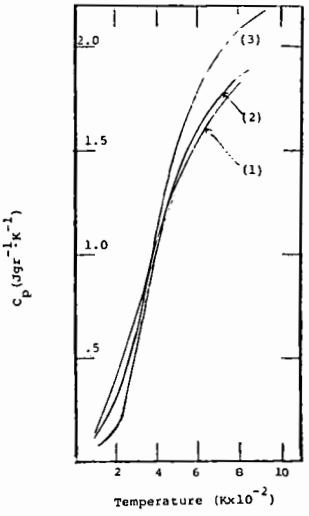

Figure 4. Demineralized Chars
(1) N. Dakota
(2) Virginia 700°C
(3) Illinois 1 Hour

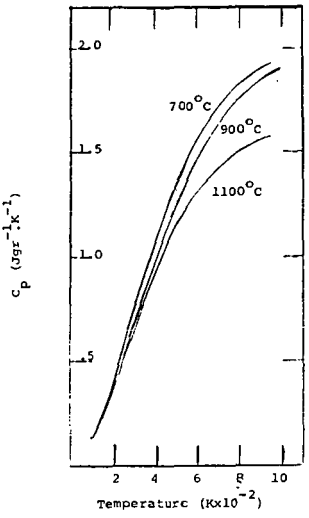

Figure 5. N. Dakota Chars

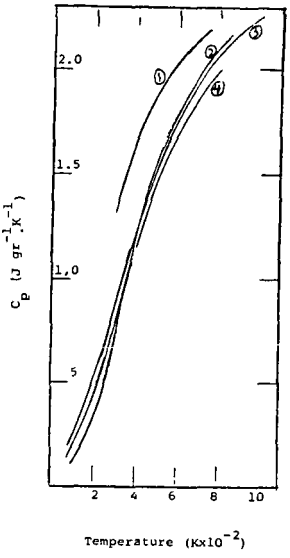

Figure 6. Illinois Chars
(1) 500°C (3) 900°C
(2) 700°C (4) 1100°C

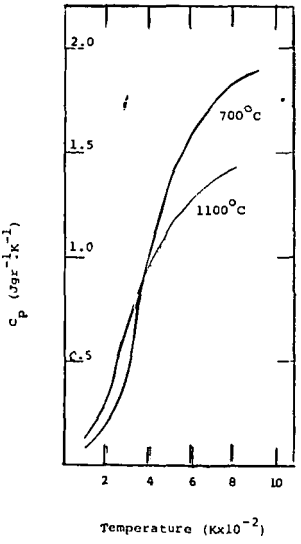

Figure 7. Virginia Chars

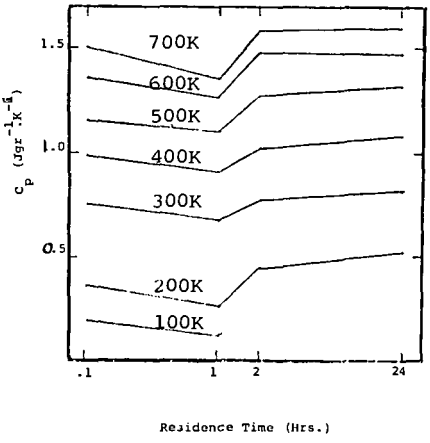

Figure 8. Virginia Chars